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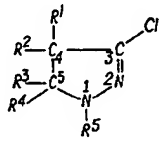
(19)

(54) 3-CHLORO-1-ARYL-2-PYRAZOLINES

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 2501 Hudson Road, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

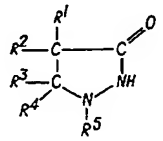
This invention relates to fluorescent chlorosubstituted pyrazoles and to their preparation and use as fluorescent materials.

According to the invention there is provided a process for the preparation of a 3-chloro-1-aryl-2-pyrazoline having the general formula:



in which R^1 to R^4 each independently of each other represents a hydrogen atom or an unsubstituted alkyl group, preferably one containing from 1 to 4 carbon atoms, an unsubstituted aralkyl group or an unsubstituted aryl group, and R^5 represents an aryl group, preferably a phenyl or naphthyl group, which may be substituted in one or more positions by radicals such as a halogen atom or an alkyl, alkoxy or alkylthio group, the alkyl, alkoxy or alkylthio substituent group preferably containing from 1 to 4 carbon atoms,

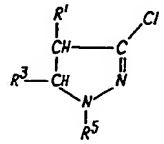
in which a 1-aryl-2-pyrazolidin-3-one having the general formula:



in which R^1 to R^5 are as defined above, is reacted with anhydrous phosphorus trichloride.

The PCl_3 is preferably in excess and acts as a solvent.

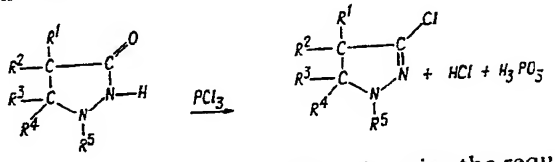
The invention also extends to certain of these 3-chloro-1-aryl-2-pyrazolines having the general formula:



in which R^1 and R^3 each independently of each other represents a hydrogen atom or an unsubstituted alkyl group, an unsubstituted aralkyl group or an unsubstituted aryl group, and R^5 represents an unsubstituted or substituted aryl group.

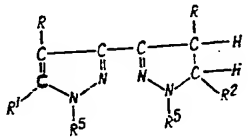
The 3-chloro-1-aryl-2-pyrazoline compounds fluoresce when irradiated with ultra violet light. Generally they are colourless or pale yellow oily liquids or low-melting solids which show strong blue fluorescence when irradiated with ultra violet light of wavelengths of from 250 to 350 mμ. They are therefore useful as, for example, optical brightening agents and fluorescent pigments. Additionally they are useful intermediates for the preparation of other fluorescent pyrazolines.

The reaction according to the invention occurs as illustrated in the following general reaction scheme:



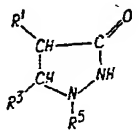
This reaction is found to proceed smoothly and to give the required 3-chloro-1-aryl-2-pyrazoline in high yields. The reaction can be very simply effected by heating the two reactants together, e.g. under reflux at the boiling point of the PCl_3 solution.

It is surprising that this reaction gives excellent yields of the required product since reacting the 1-aryl-2-pyrazolidin-3-one with the chlorinating agent phosphorus oxychloride gives only small yields of the required 3-chloro compound. In fact, the reaction with phosphorous oxychloride gives the 3-chloro compound of the invention only in small yields as a by-product of the preparation of the aryl-3,3'-pyrazolyl-2-pyrazolines which have the general formula:



in which R and R^1 each independently represent a hydrogen atom or an alkyl or aralkyl group, and R^5 is as defined above, and which are described in our copending United Kingdom Patent Application No. 6384/72 (Serial No. 1410192). The compound of the present invention can, however, be isolated as a by-product from this reaction with phosphorus oxychloride by extraction with boiling methanol.

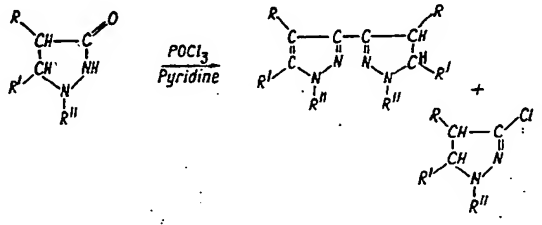
According to the preparation described in that Application aryl-3,3'-pyrazolyl-2-pyrazolines can be prepared and 3-chloro-1-aryl-2-pyrazolines prepared as a by-product by reacting a 1-aryl-pyrazolidin-3- one having the general formula:



in which R^1, R^3 adn R^5 are as defined above, under anhydrous conditions with phosphorus oxychloride in the presence of an organic base. After the completion of the reaction, the reaction mixture can be neutralised to give an insoluble precipitate which can then be purified by recrystallisation. From this purified mixture, a 3-chloro-1-aryl-2-pyrazoline of the invention can be removed as a by-product by extraction with boiling methanol.

Suitable bases for this reaction are the aromatic bases containing tertiary nitrogen atoms such as the pyridines, pyridine itself being preferred. Other pyridines blocked in the 2-position by suitable substituents, e.g. 2,6-lutidine, can however also be used.

The reaction occurs as illustrated in the following general reaction scheme:



The invention will now be illustrated by the following Examples:

Example 1.

3-Chloro-1-phenyl-2-pyrazoline

1-Phenyl-pyrazolidin-3-one (50g) was heated under reflux for four hours with phosphorus trichloride (250 ml). The excess phosphorus trichloride was distilled off and the residue poured into water.

Recrystallisation of the precipitated solid from methanol gave 3-chloro-1-phenyl-2-pyrazoline (26.0g) as pale yellow needles (melting point 99.6C) having a maximum fluorescence in chloroform at 452 nm when irradiated with ultra violet light.

Analysis (%):

Calculated for $C_9H_9N_2Cl$	: C 59.85; H 5.0; N 15.5;
Found	: C 59.6 ; H 4.4; N 15.5.

Example 2.

3-Chloro-1-(*p*-chlorophenyl)-2-pyrazoline

1-(*p*-Chlorophenyl)-pyrazolidin-3-one (3.2g) was heated under reflux for four hours with phosphus trichloride (20ml). Treatment of the reaction mixture as in Example 1 gave 3-chloro-1-(*p*-chloro-phenyl)-2-pyrazoline as colourless plates (melting point 84°C), having a maximum fluorescence in chloroform at 479 nm when irradiated with ultra violet light.

Analysis (%):

Calculated for $C_9H_8N_2Cl_2$	: C 50.52; H 3.82; N 12.83; Cl 33.0;
Found	: C 50.2 ; H 3.72; N 13.0 ; Cl 32.61.

Example 3.

3-Chloro-1-(p-fluorophenyl)-2-pyrazoline

1-(*p*-Fluorophenyl)-pyrazolidin-3-one (3.6g) was heated under reflux for six hours with phosphorus trichloride (20ml). The excess phosphorus trichloride was removed by distillation and the residue added to water. This aqueous suspension was then extracted with ether, the ethereal solution washed with dilute sodium hydroxide solution to remove any unchanged pyrazolidinone, dried with sodium sulphate and the ether removed. The residue was recrystallised from ethanol to give 3-chloro-1-(*p*-fluorophenyl)-2-plyrazoline (2.1g) as colourless rhombs (melting point 73°C). The fluorescence maximum in chloroform in 468 nm.

Analysis (%):

Calculated for $C_9H_8N_2ClF$	: C 54.76; H 3.96; N 14.25; Cl 17.97;
Found	: C 54.4 ; H 4.03; N 14.7 ; Cl 17.9 ;

Example 4.

3-Chloro-1, 5-diphenyl-2 pyrazoline

1,5-Diphenyl-pyrazolidin-3-one (5.2g) was heated under reflux for sixteen hours with phosphorus trichloride (20ml). Treatment of the reaction mixture as in Example 3 gave 3-chloro-1, 5-diphenyl-2-pyrazoline as pale yellow plates (melting point 122°C). The fluorescence maximum in chloroform was at 462 nm.

Analysis (%):

Calculated for $C_{15}H_{13}N_2C$	: C 69.9 ; H 5.48; N 10.87; Cl 13.76;
Found	: C 70.13; H 5.2; N 10.9 ; Cl 13.99.

Example 5.

3-Chloro-4-methyl-1-phenyl-2-pyrazoline

4-Methyl-1-phenyl-1-pyrazolidin-3-one (50g) was heated under reflux for 16 hours with phosphorus trichloride (250 ml). The excess phosphorus trichloride was then removed by distillation and the residue added to water. The oily product was extracted with ether the ether solution washed with dilute sodium sulphate. The ether was removed and the product distilled in vacuo to give 3-chloro-4-methyl-1-phenyl-2-pyrazoline (35g) as a pale yellow oil (boiling point [15 mm] 160—162°C), having a fluorescent maximum in chloroform at 460 nm.

Analysis (%):
Calculated for $C_{10}H_{11}N_2Cl$: C 61.70; H 5.65; N 14.40; Cl 18.25;
Found : C 62.16; H 6.30; N 14.41; Cl 18.10.

Example 6.

3-Chloro-5-methyl-1-phenyl-2-pyrazoline

5-Methyl-1-phenyl-2-pyrazoline (8.8g) was heated under reflux with phosphorus trichloride (75 ml) for 16 hours. Treatment of the resulting reaction mixture as in Example 5 gave 3-chloro-5-methyl-1-phenyl-2-pyrazoline (3.0g) as a pale yellow fluorescent oil (boiling point [15 mm] 160°C), having a fluorescent maximum in chloroform at 4.69 nm.

Analysis (%):
Calculated for $C_{10}H_{11}N_2Cl$: C 61.70; H 5.65; N 14.40; Cl 18.25;
Found : C 61.81; H 5.60; N 14.40; Cl 18.46.

Example 7.

3-Chloro-1-*p*-tolyl-2-pyrazoline

1-*p*-Tolyl-pyrazolidin-3-one (16.0g) was heated under reflux for 6 hours with phosphorus trichloride (100 ml). Treatment of the resulting reaction mixture as in Example 1 gave 3-chloro-1-*p*-tolyl-2-pyrazoline (5.3g) as pale yellow fluorescent plates (melting point 93.5°C).

Analysis (%):
Calculated for $C_{10}H_{11}N_2Cl$: C 61.70; H 5.65; N 14.40; Cl 18.25;
Found : C 62.27; H 5.78; N 14.46; Cl 17.70.

Example 8.

3-Chloro-4,4-dimethyl-1-phenyl-2-pyrazoline

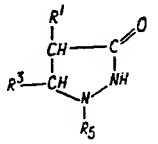
4,4-Dimethyl-1-phenyl-pyrazoline-3-one (3.8g) was heated under reflux with phosphorus trichloride (20 ml) for 6 hours. Treatment of the resulting reaction mixture as in Example 5 gave 3-chloro-4,4-dimethyl-1-phenyl-2-pyrazoline (1.5g) as a pale yellow fluorescent oil (boiling point 20 mm 165°C).

Analysis (%):
Calculated for $C_{11}H_{13}N_2Cl$: C 63.30; H 6.24; N 13.40; Cl 17.00;
Found : C 63.18; H 6.60; N 13.10; Cl 16.68.

All of these compounds prepared as in these Examples were found to fluoresce strongly when illuminated with ultra-violet light and so are useful as, for example, optical brightening agents or fluorescent pigments.

WHAT WE CLAIM IS:—

1. A 3-chloro-1-aryl-2-pyrazoline having the general formula:



in which R^1 and R^3 each independently of each othe represents a hydrogen atom or an unsubstituted alkyl group, an unsubstituted aralkyl group or an unsubstituted aryl group, and R^5 represents an unsubstituted or substituted aryl group.

2. A pyrazoline as claimed in Claim 1 in which R^5 represents a phenyl or

naphthyl group which may be substituted by one or more halogen atoms or alkyl, alkoxy or alkylthio groups.

3. 3-Chloro-1-phenyl-2-pyrazoline.

4. 3-Chloro-1-(*p*-chlorophenyl)-2-pyrazoline.

5. 3-Chloro-1-(*p*-fluorophenyl)-2-pyrasoline.

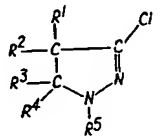
6. 3-Chloro-1,5-diphenyl-2-pyrazoline.

7. 3-Chloro-3-methyl-1-phenyl-2-pyrazoline.

8. 3-Chloro-5-methyl-1-phenyl-2-pyrazoline.

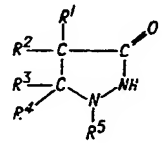
9. 3-Chloro-1-*p*-tolyl-2-pyrazoline.

10. A process for the preparation of a 3-chloro-1-aryl-2-pyrazoline having the general formula:



in which R^1 to R^4 each independently of each other represent a hydrogen atom or an unsubstituted alkyl group, an unsubstituted aralkyl group or an unsubstituted aryl group, and R^5 represents an unsubstituted or substituted aryl group,

in which a 1-aryl-2-pyrazolidine-3-one having the general formula

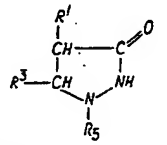


in which R^1 to R^5 are as defined above, is racted with anhydrous phosphorus trichloride.

11. A process as claimed in Claim 10 in which the phosphorus trichloride is in excess and the reaction is effected in solution in the phosphorus trichloride.

12. A process as claimed in Claim 11 in which the reaction is effected by heating the 1-aryl-2-pyrazolidin-3-one and phosphorus trichloride under reflux.

13. A process for the preparation of a 3-chloro-1-aryl-2-pyrazoline as claimed in Claim 1 in which a 1-aryl-2-pyrazolidin-3-one having the general formula:



in which R^1, R^3 and R^5 are as defined in Claim 1, is reacted under substantially anhydrous conditions with phosphorus oxychloride in the presence of an organic base, the reaction mixture is neutralized to give an insoluble mixture of the 3-chloro-1-aryl-2-pyrazole and an aryl-3,3'-pyrazolyl-2-pyrazoline and the 3-chloro-1-aryl-2-plyrazoline is extracted from the insoluble mixture with boiling methanol.

14. A process for the preparation of a 3-chloro-1-aryl-2-pyrazoline substantially as herein with reference to any of Examples 1 to 6.

15. A process for the preparation of a 3-chloro-1-aryl-2-pyrazoline substantially as herein described with reference to Example 7 or Example 8.

16. A 3-chloro-1-aryl-2-pyrazoline when prepared by a process as claimed in any of claims 10 to 15.

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